

RESERVE COPY

PATENT SPECIFICATION

416,084

Application Date: March 9, 1933. No. 7233 / 33.

Complete Left: March 9, 1934.

Complete Accepted: Sept. 10, 1934.

PROVISIONAL SPECIFICATION.



Improvements in or relating to the Production of Phosphorus Oxy-chloride.

We, IVOR ASHTON DAVIES, a British subject of Norton Hall, The Green, Norton-on-Tees, County Durham, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W. 1, do hereby declare the nature of this invention to be as follows:—

This invention relates to the production of phosphorus oxychloride by reaction between chlorine and an alkaline earth metal metaphosphate in the presence of carbonaceous reducing materials.

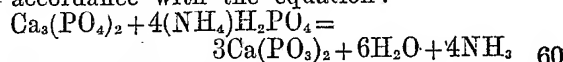
It is known to produce phosphorus oxy-chloride by passing chlorine gas over a mixture of coal and calcium metaphosphate at a raised temperature. In such a process, difficulties frequently occur owing to a relatively long induction period before the reaction commences, but we have now found that this induction period is eliminated and the course of the reaction is facilitated if the metaphosphate and the coal are both in a finely divided state and intimately dispersed in each other. We have further found that a particularly suitable way of obtaining such an intimate dispersion consists in preparing the metaphosphate in situ and simultaneously with a partial carbonisation of the coal by heating a mixture of the tribasic metal orthophosphate with an ammonium phosphate and coal. In this process the ammonium phosphate fuses and the coal also assumes a plastic state so that conditions are extremely favourable for the intimate dispersing of the metaphosphate throughout the reaction material.

According to the present invention, therefore, in the production of phosphorus oxychloride by reaction between chloride and an alkaline earth metal metaphosphate in the presence of a carbonaceous reducing agent, an intimate reaction mixture of metaphosphate and carbon is produced by heating together a mixture of tribasic metal orthophosphate with ammonium phosphate and coal.

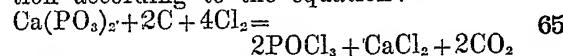
The invention will be described with reference to calcium compounds, but it will be understood that the other alkaline earth metal compounds may be used in-

stead.

Sufficient ammonium phosphate should be employed to convert the tricalcium phosphate to calcium metaphosphate in accordance with the equation:—



and sufficient coal is added to the initial reactants to comply with the requirements of the subsequent chlorinating reaction according to the equation:—



It is preferred, however, to employ more than the theoretical quantity of carbon since it is found in this manner that the mixture of metaphosphate and carbon is prevented from assuming too powdery a form during the chlorination reaction. The ratio of carbon to metaphosphate, expressed in proportions by weight, is suitably 1:1 to 1:1.5. It is preferred to employ a highly coking coal having a low ash content.

It is important that the orthophosphate and the ammonium phosphate should be intimately mixed before the reaction. The phosphates may be ground together, but preferably the orthophosphate is added in a fine state of division to a concentrated solution or melt of the ammonium phosphate and the product evaporated to dryness before, or during, the reaction.

The ammonia evolved in the preliminary step of producing calcium metaphosphate may, if desired, be utilised by absorption in dilute phosphoric acid or crude phosphoric acid containing liquors, such as are obtained in the extraction of rock phosphate, and the products worked up to give further quantities of ammonium phosphate.

A further advantage of the present process resides in the reduction in the quantity of fluorine and silica present as impurities in the initial reactants before the chlorination step. We have found that fluorine and silica compounds inhibit the production of phosphorus oxychloride from chlorine and calcium metaphosphate and they are, to a certain extent, responsible for the induction period. According to the present invention, however, we

[Price 1/-]

Price 4s 6d.

have found that in the initial step they combine with part of the ammonia evolved from the decomposition of the ammonium phosphate with the formation of volatile compounds, such as ammonium fluoride and ammonium silica-fluoride, which may be recovered in any known or suitable manner.

EXAMPLE

- 10 A phosphate rock containing 76% tricalcium phosphate together with metallic carbonates and fluorides as impurities was finely ground and 6 parts by weight of the ground product
15 were mixed with 11 parts by weight of a pulverised coking coal containing less than 8% ash. The mixture was added to 12 parts by weight of mono-ammonium

phosphate in the form of a concentrated aqueous solution and the suspension evaporated to a slurry and granulated. The granules were then carbonised at a temperature of the order of 700° C., thus affording a product consisting of an intimate mixture of calcium metaphosphate and carbon in the proportion of approximately 4:3 by weight. This product was then treated in a stream of chlorine gas at a temperature of 650—750° C. and 15—16 parts by weight of phosphorus oxychloride were obtained.

Dated the 9th day of March, 1932.

E. A. BINGEN,
Imperial Chemical House, Millbank,
London, S.W. 1.
Solicitor for the Applicants.

COMPLETE SPECIFICATION.

Improvements in or relating to the Production of Phosphorus Oxychloride.

- We, IVOR ASHTON DAVIES, a British subject of Norton Hall, The Green, Norton-on-Tees, County Durham, and
35 IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W. 1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

- This invention relates to the production of phosphorus oxychloride by reaction
40 between chlorine and an alkaline earth metal metaphosphate in the presence of carbonaceous reducing materials.

- It is known to produce phosphorus oxychloride by passing chlorine gas over a mixture of coal and calcium metaphosphate at a raised temperature of the order of 300° C. In such a process, difficulties frequently occur owing to a relatively long induction period before the reaction commences, and also owing to the slowing down of the reaction as a result of the formation of calcium chloride. We have found that the induction period is eliminated and the course of the reaction is facilitated if the metaphosphate and the coal are both in a finely divided state and intimately dispersed in each other. A particularly suitable way of obtaining such an intimate dispersion consists in
60 preparing the metaphosphate in situ and simultaneously with a partial carbonisation of the coal, by heating a mixture of the tribasic metal orthophosphate with ammonium phosphate and coal. In this
70 process the ammonium phosphate fuses

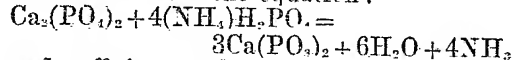
and the coal, if it is a coking coal also assumes a plastic or pasty state so that conditions are extremely favourable for the intimate dispersing of the metaphosphate throughout the reaction material.

We have also found that by carrying out the reaction at 500—750° C. the harmful effect of the calcium chloride produced in the reaction is largely neutralised, since the calcium chloride partly melts and in this state causes less interference with the reaction between the chlorine and the metaphosphate.

According to the present invention, therefore, in the production of phosphorus oxychloride by reaction between chlorine and an alkaline earth metal metaphosphate in the presence of a carbonaceous reducing agent, we employ a reaction temperature of 500—750° C. and preferably at least 650° C. Preferably an intimate reaction mixture of metaphosphate and carbon is produced by heating together a mixture of tribasic metal orthophosphate with ammonium phosphate and coal.

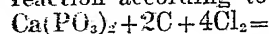
The invention will be described with reference to calcium compounds but it will be understood that the other alkaline earth metal compounds may be used instead.

Sufficient ammonium phosphate should be employed to convert the tricalcium phosphate to calcium metaphosphate in accordance with the equation:



and sufficient coal is added to the initial reactants to comply with the require-

ments of the subsequent chlorinating reaction according to the equation:



- 5 It is preferred, however, to employ more than the theoretical quantity of carbon since it is found in this manner that the mixture of metaphosphate and carbon is prevented from assuming too powdery a form during the chlorination reaction. 10 The ratio of carbon to metaphosphate, expressed in proportions by weight, is suitably 1:1 to 1:1.5. It is preferred to employ a highly coking coal having a 15 low ash content.

- It is important that the orthophosphate and the ammonium phosphate should be intimately mixed before the reaction. The phosphates may be ground together. 20 but preferably the orthophosphate is added in a fine state of division to a concentrated solution or melt of the ammonium phosphate and the mixture evaporated to dryness. The coal may be mixed with 25 the product which has been evaporated to dryness or with the finely divided orthophosphate which is added to the concentrated solution or melt of ammonium phosphate.

- 30 The ammonia evolved in the preliminary step of producing calcium metaphosphate may, if desired, be utilised by absorption in dilute phosphoric acid or crude phosphoric acid containing liquors 35 such as are obtained in the extraction of rock phosphate, and the products worked up to give further quantities of ammonium phosphate.

- A further advantage of the present process resides in the reduction in the quantity of fluorine and silica present as impurities in the initial reactants before the chlorination step. We have found that fluorine and silica compounds inhibit 45 the production of phosphorus oxychloride from chlorine and calcium metaphosphate and they are, to a certain extent, responsible for the induction period. According to the present invention, however, we 50 have found that in the initial step they combine with part of the ammonia evolved from the decomposition of the ammonium phosphate with the formation of volatile compounds, such as ammonium fluoride and ammonium silica-fluoride which may 55 be recovered in any known or suitable manner.

EXAMPLE

- 60 A phosphate rock containing 76% tricalcium phosphate together with metallic carbonates and fluorides as impurities was finely ground and 6 parts by weight of the ground product were mixed with 11 parts by weight of 65 a pulverised coking coal containing less

than 8% ash. The mixture was added to 12 parts by weight of mono-ammonium phosphate in the form of a concentrated aqueous solution and the suspension evaporated to a slurry and granulated. 70 The granules were then carbonised at a temperature of the order of 700° C., thus affording a product consisting of an intimate mixture of calcium metaphosphate and carbon in the proportion of approximately 4:3 by weight. This product 75 was then treated in a stream of chlorine gas at a temperature of 650—750° C. and 15—16 parts by weight of phosphorus oxychloride were obtained on cooling the 80 effluent gases.

The term "ammonium phosphate" as used herein means mono-, di-, or tri-ammonium orthophosphate, the last two of which decompose on heating to yield 85 mono-ammonium phosphate.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we 90 claim is:—

1. A process for the production of phosphorus oxychloride which comprises reacting an alkaline earth metal metaphosphate with chlorine in the presence of a carbonaceous reducing agent at a temperature 95 of 500 to 750° C. and preferably at least 650° C.

2. A process for the production of phosphorus oxychloride which comprises preparing an intimate reaction mixture of an alkaline earth metal metaphosphate and carbon by heating together a mixture of tribasic alkaline earth metal orthophosphate with ammonium phosphate and coal, and subsequently treating the mixture with chlorine at a raised temperature. 105

3. A process as set forth in Claim 2, in which an excess of carbon is used over that theoretically required, the ratio of carbon 110 to metaphosphate being from 1:1 to 1:1.5 expressed in parts by weight.

4. A process for the production of phosphorus oxychloride which comprises mixing a finely divided alkaline earth metal orthophosphate with a concentrated solution or melt of ammonium phosphate, evaporating the mixture to dryness, mixing the product with coal, carbonising the product and then treating the carbonised product with chlorine at a temperature 120 of 500—750° C., and preferably at at least 650° C.

5. A process for the production of phosphorus oxychloride which comprises mixing a finely divided alkaline earth metal orthophosphate and finely divided coal with a concentrated solution or melt of ammonium phosphate, evaporating the mixture to dryness, carbonising the pro- 125 130

duct and then treating the carbonised product with chlorine at a temperature of 500—750° C. and preferably at least 650° C.

5 6. A process as set forth in Claim 5, in which the mixture of orthophosphate, ammonium phosphate and coal is granulated prior to carbonisation.

10 7. A process as set forth in Claim 5, in which the coal is a coking coal which

becomes more or less pasty on heating to carbonising temperatures.

8. Phosphorus oxychloride whenever obtained by the process set forth in any of claims 1—7.

Dated the 9th day of March, 1934.

E. A. BINGEN

Imperial Chemical House, Millbank,
London, S.W. 1.

Solicitor for the Applicants.

15